ALS Standard Operating Procedure

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DOCUMENT TITLE:	SAMPLE EXTRACTION AND PREPARATION OF PESTICIDES AND PCB SAMPLES ACCORDING TO EPA COMPENDIUM METHODS TO-4A AND TO-10A
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STANDARD OPERATING PROCEDURE

SAMPLE EXTRACTION AND PREPARATION OF PESTICIDES AND PCB SAMPLES ACCORDING TO EPA COMPENDIUM METHODS TO-4A AND TO-10A

EPA TO-4A AND TO-10A

SOP ID:	SVP-TO4A	Rev. Number:	08.0	Effective Date:	01/31/2014

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SAMPLE EXTRACTION AND PREPARATION OF PESTICIDES AND PCB SAMPLES ACCORDING TO EPA COMPENDIUM METHODS TO-4A AND TO-10A

1) Scope and Applicability

1.1 This document is intended to provide a procedure for sample preparation used in the determination of Chlorinated Pesticides and Polychlorinated Biphenyls (PCBs) in ambient air using Compendium Methods TO-4A and TO-10A. This method utilizes both a filter and a backup cartridge (PUF) per client specific requirements, which provides for efficient collection of most pesticides and PCBs.

1.2 The approximate number of extractions (including sample preparation) that can be performed at any one time is twenty.

2) Summary of Procedure

2.1 The certified filters and sorbent cartridges (containing PUF) are extracted together by Soxhlet extraction, (EPA Method 3540) utilizing the appropriate solvent in order to permit an accurate measurement of both Chlorinated Pesticide and Polychlorinated Biphenyl air concentrations. Surrogates are added to each sample prior to extraction to measure the effectiveness of the preparation process. Once the sample has been on the Soxhlet extractor for a period of 16 hours the extract is concentrated by a Turbo-Vap evaporator to 10mL prior to the analysis by gas chromatography with electron capture detection (GC/ECD).

3) Definitions

3.1 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.2 Field Sample A sample collected and delivered to the laboratory for analysis.

3.3 Batch QC Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS), or Laboratory Duplicate (LD), etc.

3.4 Method Blank (MB) An analyte-free matrix to which all reagents are added in the same quantities or proportions as used in field sample processing and is carried through the entire analytical process. It is used to evaluate the process for contamination from the laboratory.

3.5 Laboratory Control Sample (LCS) A laboratory control sample is an analyte-free matrix to which a known quantity of analyte(s) is (are) added. The LCS is subjected to the same processing as field samples and is carried through the entire analytical process. The percent recovery of the analyte(s) in the LCS is used to assess method performance. Certain programs and projects require analysis of a laboratory control sample duplicate (LCSD).

3.6 Surrogate Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatographic response, but which are not normally found in environmental samples. The purpose of the surrogate is to monitor unusual matrix effects, gross sample preparation and analysis errors. These compounds are spiked into all blanks, standards, samples and LCS prior to analysis. Percent recoveries are calculated for each surrogate. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

4) Health and Safety Warnings

4.1 Safety Data Sheets (SDS)

The toxicity of each reagent used in this procedure may not be precisely defined. Safety data sheets are available and should be reviewed as part of employee training. Care should be taken when handling standard material in neat or highly concentrated form.

4.2 Protective Clothing

Personal protective clothing (safety glasses, gloves and lab coat) are required when preparing samples, handling standard material in neat form, or performing maintenance on pressurized systems.

4.3 Pressurized Gases

The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

4.4 Pollution Prevention and Waste Management The following wastes are generated during the TO-4A/TO-10A analysis: neat, intermediate and working standards, sample extracts and rinsate from syringes. Used standards and extracts (hexane/ethyl ether) are stored in refrigerators until they are lab packed and sent for off-site disposal. Rinsate (methanol, hexane/ethyl ether) generated during cleaning of syringes is collected in the waste solvent container located under the prep lab's hood. This waste is consolidated with other flammable solvent waste. All waste streams are transported off-site and disposed of in accordance with environmental regulations by an approved waste hauler. Uniform hazardous waste manifests from the waste handling company are stored according to the *SOP for Waste Disposal*.

5) Cautions

5.1 Periodically check condenser fittings to ensure that none are leaking water. Also, inspect all glassware before using for cracks and chips that would hinder the integrity of the extraction system.

6) Interferences

6.1 Sample Contamination

Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it and then high purity acetone and hexane. These rinses shall be followed by detergent washing with hot water and rinsing with copious amount of tap water and several portions of de-ionized water. The glassware must be thoroughly rinsed with methanol and then rinsed with hexane and allowed to dry. The glassware may then be heated at 400ºC for four hours to remove trace organics. The glassware cleaning is performed in accordance with the *SOP for Glassware Cleaning*. After drying and rinsing, glassware must be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.

Note: Volumetric glassware must not be heated; rather it should be solvent rinsed with acetone and hexane. Also, all glassware should be thoroughly solvent rinsed using the appropriate solvent for extraction prior to each use.

7) Personnel Qualifications and Responsibilities

7.1 It is the responsibility of the technician to perform the procedure according to this SOP and to complete all required documentation. This procedure shall be performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory.

7.2 Review and approval of the preparation data is performed by either the analyst or department supervisor.

7.3 Training shall be conducted in accordance with the *SOP for Training Policy.* An initial demonstration of proficiency shall be performed prior to independent analysis of samples (Attachment 1). A continuing demonstration of proficiency must be performed annually.

8) Sample Collection, Handling, and Preservation

8.1 Samples must be refrigerated at less than or equal to 4ºC for up to 7 days prior to extraction and 40 days to analysis of extract. Samples are packed with blue ice for transport to and from the extraction laboratory. The technician must document custody through LIMS or an internal chain of custody form.

Note: The methods EPA TO-4A and TO-10A specifically state that samples and extracts be stored at <4˚C, however a possible modification to this requirement is that they may be stored up to 6˚C (4˚C ± 2˚C).

9) Equipment and Supplies

9.1 Apparatus and Equipment

- Quartz fiber filter- 102 millimeter binderless quartz microfiber filter
- Polyurethane foam (PUF) plugs- The PUF should be of the polyurethane type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge.
- Teflon® end caps – for sample cartridge
- Aluminum foil
- Hexane, reagent grade
- Glass container
- Soxhlet apparatus
- Acetone
- Diethyl ether
- hexane
- Turbo-vap
- Drying column
- Anhydrous granular sodium sulfate
- Erlenmeyer flask
- Boiling chips

10) Standards and Reagents

10.1 Solvents

Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences.

10.1.1 Acetone 99.9%

10.1.2	Hexane	99.9%
10.1.3	Diethyl Ether	99.9%

10.2 Extraction Solvent Mixture

The extraction solvent is 10% Ether in Hexane and shall be prepared using the following procedure.

- Take a 4L bottle of Hexane (Section 10.1.2), decant off 400mL and deposit in the Hexane solvent reservoir used to rinse glassware.
- Add 400mL of Diethyl Ether (Section 10.1.3) to the 4L Hexane bottle. Invert 3X and either use immediately or store properly until ready to use.

10.3 Standards and Surrogates

The surrogate, laboratory control sample and matrix spikes required for this method shall be prepared according to the procedures detailed in the analytical SOP for EPA Compendium Method TO-4A/TO-10A.

11) Method Calibration

11.1 Not Applicable

12) Sample Preparation/Analysis

12.1 Sufficient raw data records must be retained of the sample preparation including solvent, and amount used, lot number, sample identification, technician's initials, and surrogate identification and amount spiked. All information must be entered onto the sample extraction log and it shall be complete and accurate.

12.2 Preparation/Certification of Sampling Media

This portion of the procedure describes information regarding the cleaning of the filter, sorbent, and filter/sorbent cartridge assembly. The separate batches of filters and sorbents are extracted with the appropriate solvent. At least one PUF and filter from each cleaning batch, or 10 percent of the batch, whichever is greater, must be tested and certified before the batch shall be considered for field use. The PUF initial cleaning procedure is described below (Section 12.2.2).

Note: The same solvent lot must be used throughout both cleaning and certification procedure.

12.2.1 Bake the Whatman quartz filters at 450°c for 4 hours before use.

12.2.2 Initial cleaning

For initial cleaning (new media), place the PUF plugs in a Soxhlet apparatus and extract with 600mL of acetone for 16 hours at approximately 4 cycles per hour. Alternatively, soak the new media (PUF) in acetone for 24 hours prior to Soxhlet extraction with hexane/ether.

12.2.3 Following initial cleaning, the PUF plugs are placed in a cartridge and Soxhlet extracted for 16 hours at approximately 4 cycles per hour with 600mL of the 10% Ether in Hexane. All previously used PUF/cartridges only need extracted once with the 10% Ether in Hexane and do not require the initial acetone clean up that is done for new media.

12.2.4 Concentrate the PUF/cartridge extracts to a final volume of 10mL.

12.2.5 Remove the PUF/cartridges and place under a hood and cover with aluminum foil and allow to dry at room temperature overnight.

12.2.6 Wrap the sampling cartridge with aluminum foil and place in a clean screw-capped jar.

12.2.7 Submit all PUF/cartridge extracts from each batch to the analyst for analysis.

12.2.8 10% of batch cleaned cartridges must pass the technical acceptance criteria before the batch is considered acceptable for field use.

12.3 Spiking Laboratory Surrogates

Laboratory surrogates shall be added to all samples, method blanks and batch QC samples just prior to extraction. Refer to the analytical SOP for EPA Compendium Method TO-4A/TO-10A for the surrogate preparation procedure.

12.4 Method Blank

A designated PUF cartridge shall be taken and spiked with 50µL of the 20µg/mL surrogate solution. The cartridge must be taken through the extraction process described in Section 12.7 of this document.

12.5 Laboratory Control Sample/Laboratory Control Sample Duplicate

A designated PUF shall be taken and spiked with 50µL of the 20µg/mL surrogate solution and with 50µL of the 20µg/mL pesticide spiking solution or 50µL of the 100µg/mL PCB spiking solution. The cartridge must then be handled identically to actual samples and taken through the extraction process detailed in Section 12.7. Refer to the analytical SOP for EPA Compendium Method TO-4A/TO-10A for the spike preparation procedure.

12.6 Preparation Batch Guidelines

- The number of samples in a preparation batch shall not exceed 20.
- Laboratory duplicate (LD) samples are considered samples.
- There must be at least one duplicate sample (LCSD) extracted to access batch precision.
- The laboratory method blank must be extracted at a frequency of 1 in 20 or fewer samples.
- All field samples must be extracted and analyzed with an associated LCS.
- Duplicate field samples should be extracted when they are submitted.
- A laboratory reagent blank must be analyzed per reagent (per new lot received) as a measure of purity.
- All steps in the analytical procedure must use the same reagents, standards, surrogates, equipment, apparatus, glassware, and solvents that would also be used for sample analysis.

12.7 Sample Extraction Procedure

The sample extraction log should be initiated prior to beginning the extraction procedure. It is important to ensure that the actual Soxhlet position is mirrored on the log in order to make any notations regarding a particular sample. Also, it is good practice to fill in the spike volumes on the log as each spike is added.

- Before removing the cartridges from their glass jars, rinse the appropriate number of round bottom flasks (with boiling chips) and Soxhlet extractors with hexane.
- Label each round bottom flask with the sample identification number and fill with approximately 200mL of 10% ether in hexane.
- Remove each cartridge and filter (if available) from the containers and spike with 50µL of 20µg/mL surrogate solution.

- Place the cartridge inside of the Soxhlet extractor and connect to the round bottom flask.
- Add 500mL of the 10% ether in hexane. Attach the water condenser to the Soxhlet apparatus for cooling purposes.
- After all samples have been spiked and connected to the water condensers, switch the water valve to the "on" position and adjust so that a steady stream of water comes out of the drain line.
- Turn "on" the heating mantles so that 4 cycles/reflux per hour occurs for 16 hours.
- Allow the samples to cool following the 16-hour extraction prior to the concentration process.
- Concentrate the samples by using a Zymark turbo-vap system. The turbo-vap is combination water bath/gas "blow down" concentrating system.
- Set the water bath at 60 degrees Celsius and the flow of ultra-high purity nitrogen at 7.5psi.
- Fill the concentrator tubes 2/3 of the way full to avoid "splashing" when condensing first begins.
- Allow the extract to concentrate to just below 10mL.
- Transfer the extract to a clearly labeled 10 ml volumetric flask.
- Rinse the walls of the turbo-vap tubes using small aliquots of hexane and disposable pipets and transfer to the volumetric flask. Bring up to a 10ml final volume.
- Once all samples are labeled, complete the extraction logbook with the final extract concentration, comments, technician's initials, and extraction date.
- Transport the extracts back to the lab via a small cooler containing blue ice for cooling purposes.
- Relinquish extracts to the analyst.

13) Troubleshooting

13.1 Prepare new standards, check maintenance, etc. Refer to Section 16 of this SOP for additional troubleshooting details.

14) Data Acquisition

14.1 Not Applicable

15) Calculation and Data Reduction Requirements

15.1 The analyst must review and approve all extraction data at the time of receipt. The reviewer shall review all information including solvent type and amount, sample identification, batch QC, surrogate use, comments, etc. This log shall show the date and initials of the analyst(s) and is retained physically or electronically.

16) Quality Control, Acceptance Criteria, and Corrective Action

16.1 Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance Corrective Action*, where appropriate. This includes documenting any problems with the extraction procedure, breaking a sample, extracting to dryness, etc. All corrective actions must be documented either by initiating an NCAR or making a notation on the sample extraction log. This is to ensure an out of control result is contributed to an assignable cause and it is properly documented.

16.2 Compromised Sample

When a sample has been compromised, for example, an extract or sample container has been dropped and broken or when an extract is concentrated to dryness, a non-conformance corrective action report (NCAR) must be generated and the project

manager and client informed. This NCAR must be retained in the job file and case narrative.

16.3 Contamination

If contamination is suspected from either glassware that was not properly cleaned or carryover from high level samples, a non-conformance corrective action report (NCAR) must be generated. The client must be notified and any discrepancies noted in the job file and report case narrative.

16.4 Sample's Holding Time Expired

Notify the analyst of any missed holding time, so that the customer may be notified. Documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A decision may be made to abort the sample extraction process, if this is the case, return the sample to the laboratory. If sample extraction is to continue, make a notation on the extraction log of the missed holding time and the decision to proceed by the client.

16.5 Media Certification Failure

If compounds are detected above the reporting limits, all associated cartridges must be re-cleaned and analyzed for certification consideration.

17) Data Records Management

17.1 All data resubmittal forms and job documentation including Service Requests, Chain of Custody forms, Sample Acceptance Check forms and hardcopy electronic mail messages must be filed in the project file. Final reports, revised reports, and final invoices are stored electronically.

17.2 All laboratory and client documentation must be retained for a minimum of five years.

18) Contingencies for Handling Out of Control Data

18.1 Refer to Section 18 in the analytical *SOP for Determination of Pesticides and Polychlorinated Biphenyl (PCBs) in Ambient Air by GC/ECD per EPA Compendium Methods TO-4A and TO-10A*; SOP ID SVO-TO4A.

19) Method Performance

19.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as specified in the determinative method SOP.

19.2 Laboratory Surrogate Spikes

Each field sample and QC sample (LCS/LCSD; Method Blank) is spiked with a laboratory surrogate(s). The surrogate recovery is used to assess method and extraction performance.

20) Summary of Changes

Table 20.1

Revision Number	Effective Date	Document Editor	Description of Changes
08.0	01/31/14	C. Humphrey	Major document format revision. SOP updated using current ALS SOP template. New cover page and footer.

			Sections reorganized. See list of specific changes below.

Section 1.2 Changed number of extractions to twenty
Section 4 Renamed "Health and Safety Warnings"; Previously Sections 6.0 and 15.0
Section 4.1 Updated to Safety Data Sheets (SDS)
Section 5 Renamed "Cautions"; Previously Section 10.0
Section 6 Previously Section 5.0
Section 7 Renamed "Personnel Qualifications and Responsibilities"; Previously Sections 4.0 and 18.0
Section 8 Renamed "Sample Collection, Handling, and Preservation"; Previously Section 7.0
Section 9 Renamed "Equipment and Supplies"; Previously Section 8.0
Section 10 Renamed "Standards and Reagents"; Previously Section 9.0
Section 11 Renamed "Method Calibration"
Section 12 Renamed "Sample Preparation/Analysis"; Information previously in Section 11.0
Section 12.2.8 Updated to include 10% of batch criteria
Section 12.6 Updated to reflect preparation batch verses analytical batch
Section 12.7 Updated 13th and 14th bullets
Section 13 Renamed "Troubleshooting"; New Section
Section 14 Renamed "Data Acquisition"
Section 15 Renamed "Calculation and Data Reduction Requirements"; Information previously in Section 13.0
Section 16 Renamed "Quality Control, Acceptance Criteria and Corrective Action"; Information previously in Sections 12.0 and 16.0
Section 17 Renamed "Data Records Management"; New Section
Section 18 Renamed "Contingencies for Handling Out of Control Data"; Previously Section 17.0
Section 19 Renamed "Method Performance"; Previously Section 14.0
Section 20 Renamed "Summary of Changes"; Previously Section 22.0
Section 21 Renamed "Reference and Related Documents"
Section 21 Changed "SOP Code" to "SOP ID" throughout section
Section 22 Renamed "Appendix"; Previously Section 23.0

Section previously 19.0 titled "Method Modifications" - information moved to section 8.

21) References and Related Documents

21.1 Compendium of Methods for the Determination of Toxic Qrganic Compounds in Ambient Air, *Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MS),* Compendium Method TO-4A, Second Edition, January 1999.

21.2 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, *Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MS),* Compendium Method TO-10A, Second Edition, January 1999.

21.3 *SOP for Batches and Sequences*, SOP ID ADM-BATCH_SEQ

21.4 *SOP for Making Entries onto Analytical Records*, SOP ID CE-QA007

21.5 *SOP for Nonconformance and Corrective Action*, SOP ID CE-QA008

21.6 *SOP for Handling Consumable Materials*, SOP ID ADM-CONSUM

22) Appendix

22.1 Attachments

Attachment 1 – Training Plan

Attachment 2 – Extraction Benchsheet

Attachment 1

Training Plan

Training Plan for Preparation of Air Samples for Determination of PCBs and Pesticides

Trainee_____ Trainer_____ Completion Date:_____

1. Read SOP — Trainer ____ Trainee ____ Date _____

2. Read Methods: EPA Compendium Method TO-4A and TO-10A — Trainer ____ Trainee ____ Date _____

3. Demonstrated understanding of the scientific basis of extraction — Trainer ____ Trainee ____ Date _____

4. Demonstrated familiarity with related SOPs — Trainer ____ Trainee ____ Date _____
   - SOP for Batches and Sequences; Rev. ____
   - SOP for Making Entries onto Analytical Records; Rev. ____
   - SOP for Significant Figures; Rev. ____
   - SOP for Nonconformance and Corrective Action; Rev. ____
   - SOP for Analysis of PCBs and Pesticides in Air by GC/ECD; Rev. ____
   - SOP for Glassware Cleaning; Rev. ____
   - SOP for Waste Disposal; Rev. ____

5. Observe performance of SOP — Trainer ____ Trainee ____ Date _____
   - ___Spiking surrogates
   - ___Sample extraction apparatus setup
   - ___Sample extraction and extract preparation
   - ___Sample transport and documentation
   - ___Apparatus breakdown

6. Perform SOP with supervision — Trainer ____ Trainee ____ Date _____
   - ___Spiking surrogates
   - ___Sample extraction apparatus setup
   - ___Sample extraction and extract preparation
   - ___Sample transport and documentation
   - ___Apparatus breakdown

7. Independent performance of the SOP — Trainer ____ Trainee ____ Date _____
   - ___Spiking surrogates
   - ___Sample extraction apparatus setup
   - ___Sample extraction and extract preparation
   - ___Sample transport and documentation
   - ___Apparatus breakdown
   - ___Initial demonstration of competency (selection at the discretion of Laboratory Director and/or QAM)
     - "work cell" analyst:_____
     - ___ Method Detection Limit Study; or
     - ___ Single blind sample; or
     - ___ Four consecutive laboratory control samples

8. Instrument operation and maintenance — Trainer ____ Trainee ____ Date _____
   - ___TurboVap II
   - ___Water Bath
   - ___Six position combination heating mantles

Attachment 2

Extraction Benchsheet

ALS Environmental
TO-4A/TO-10A SAMPLE EXTRACTION LOG

DATE : ____ / ____ / 201____ **ANALYSIS :** TO-4A /TO-10A **EXTRACTION METHOD:** Soxhlet

Batch Type: ____ Sample Extraction _____ Cleaning/Certification
Cleaning/Certification Matrix: ___XAD-2® ___PUF ___PUF/XAD-2®/Filter
Filter Lot #:_____ *Cartridge Volume*: _____ High _____ Low
Surrogate Spike – Conc.: _____ug/mL; ID: S_____
LCS – Conc.: _____ug/mL; ID: S_____

Solvent: __90%/10% n-Hexane/Ether __$MeCl_2$ __Acetone
Solvent ID: S_____ Lot#:_____ Lot#:_____
Solvent ID: S_____ Lot#:_____ Lot#:_____
Solvent ID: S_____ Lot#:_____ Lot#:_____
Cleanup Performed: Y / N *Solvent Exchange*: Y / N
N_2 Flow: _____ *Concentrator Temperature*: _____

Pos.	Laboratory Identification	Client ID	Cartridge Identification	Spike (uL) - Surrogates	Spike (uL) – LCS / MS	Final Vol. (mL)	Comments

Extraction By: _____ Date: _____ Start Time: _____ Stop Time: _____ Extracts Received By: _____ Date: _____

Log Sheet Approved By: _____ **Date:** _____